New Nouveau
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Open File Report 91-15

A PRELIMINARY EVALUATION TO DETERMINE WHETHER SUPPORTED LIQUID MEMBRANE TECHNOLOGY IS A VIABLE TECHNIQUE TO RECOVER METALS FROM ACID MINE DRAINAGE

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Natural Resources and Energy

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PROJECT #: 1003

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SUMMARY

Heavy metals such as zinc and copper dissolved in discharge streams contribute to the global problem of acid mine drainage and account for significant metal losses. It was postulated that supported liquid membrane technology (a variation of solvent extraction) could be used to recover the dissolved heavy metals from these streams prior to tailings impoundment or other effluent treatment processes. Revenues obtained from the sale of the metals could be used to offset the costs of treatment. Potential benefits include simplification of waste stream handling, mitigation of potential adverse environmental problems and an increase in overall metal recoveries.

A literature search indicated that supported liquid membrane technology had been used to recover metals particularly zinc from waste streams.

Limited laboratory testing was carried out using a membrane mediated system. Recoveries of over 95% of the zinc in a sample of acid mine drainage from a site in northern New Brunswick were achieved. The technique was demonstrated to be technically viable based on preliminary bench-scale testing.

RÉSUMÉ

Les métaux lourds, comme le zinc et le cuivre, dissous dans les émissaires, contribuent au problème global du drainage minier acide et ils représentent des pertes substantielles de métaux. On a postulé que la technologie des membranes liquides renforcées (une variante de l'extraction des solvants) pourrait servir à récupérer les métaux lourds dissous de ces cours d'eau avant de recourir aux bassins de résidus ou à d'autres processus de traitement des effluents. Les revenus tirés de la vente des métaux pourraient servir à compenser les coûts du traitement. Parmi les avantages possibles du procédé, on note la simplification du traitement des émissaires, l'atténuation des problèmes environnementaux négatifs potentiels et une récupération générale accrue des métaux.

Une recherche documentaire a révélé que l'on a déjà eu recours à la technologie des membranes liquides pour récupérer des métaux, en particulier du zinc, de cours d'eaux usées.

Des essais de laboratoire limités ont été réalisés à l'aide du système assisté par membranes. On a obtenu des taux de récupération de plus de 95 p. 100 du zinc dans un échantillon de drainage minier acide d'un site du nord du Nouveau-Brunswick. Il a été démontré que la technique était techniquement viable d'après des essais préliminaires en laboratoire.

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1.0 INTRODUCTION

Many streams from mine sites in New Brunswick contain significant quantities of heavy metals (eg. zinc, copper, nickel) which might be recovered. At present, the effluent is usually treated by adding either lime or limestone to the stream and precipitating dissolved heavy metals as hydroxides and sulphate as gypsum. One novel method to recover dissolved metals is solvent extraction using supported liquid membrane technology. Supported liquid membrane technology appears to offer economic potential in recovering dissolved metals. The technique has not been tried in the mining industry although variations of it are used in the food and pharmaceutical industries. The objective of this study, which was funded by the Mineral Development Branch of the New Brunswick Department of Natural Resources and Energy, is to determine whether supported liquid membrane technology is a viable method for recovering metals, particulary zinc, from acidic drainage streams. Experiments were carried out with a laboratory membrane mediated test unit.

1.1 Supported Liquid Membrane Technology

The most common way of dealing with acidic streams is to treat the effluent with either lime or limestone. The calcium combines with the sulphate to form gypsum which precipitates. Then, as the pH becomes more alkaline the dissolved metal ions precipitate as their hydroxides. These precipitates are very fine and are hard to handle. Also, being slow to settle, they require large impoundment areas.

If the high dissolved heavy metal values could be recovered from these streams, it might alleviate the cost of treating the stream and might simplify its treatment. The most important metal in the AMD streams of northern New Brunswick appears to be zinc.

A recent innovation has been the discovery of liquid membrane technology. This technology appears to offer a number of advantages over conventional solvent extraction including:

- elimination of organic losses in the aqueous phase
- no necessity to scrub the organic phase
- no crud formation
- low investment in organic reagents

Other advantages with the technology include better pH control and the option to use extractants that might not otherwise be used because of their expense, or low interfacial tension, or small density differences or higher than normal solubility in the aqueous phase.

Membrane mediated solvent extraction utilises a polymeric membrane which acts as an interface between the organic phase and the aqueous phases (see Figure 1). The membrane will be wetted usually by the aqueous phase, therefore, to eliminate transfer of the wetting fluid across the membrane, the non wetting phase needs to be maintained at a higher pressure than the wetting phase. The polymeric film is generally made of polypropylene, polysulphone or other polymeric materials and has pore sizes which range from 0.02 to 1 microns.

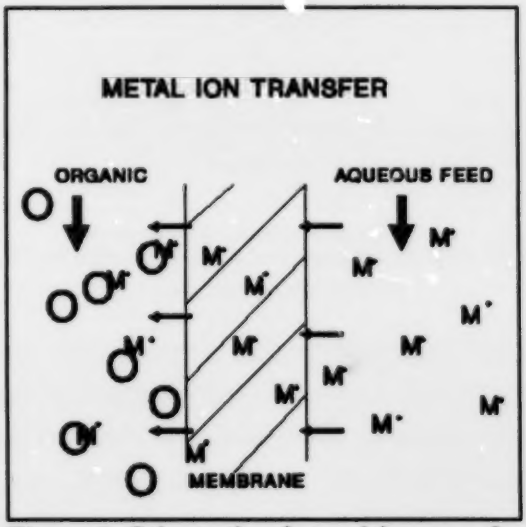


Figure 1: Schematic of metal ion transfer for a membrane mediated system.

To function, it is necessary for the distribution ratio of the metal solute between the organic phase and the aqueous feed to be as high as possible and for the distribution ratio between the organic phase and the aqueous strip solution to be as low as possible. From this, it follows that metal species can be transported across the membrane against their concentration gradient i.e. from low concentration to high concentration so that all the recoverable metal can be removed from the feed solution. For an acidic extractant, the difference in the distribution ratios is achieved by a pH gradient and for neutral or basic extraction the difference is obtained through a counter-ion gradient. In addition, it follows that very high concentration ratios can be achieved by using a small volume of strip solution compared to the volume of feed solution.

Commercial application of membrane technology appears to have been confined to the pharmaceutical and food industries. Using a membrane provides better purity control when manufacturing drugs. In the food industry, the dealcoholization of beer and wine is becoming an important application. Verbal communication (W.A. Rickleton of Cyanamid Canada) indicated that an SLM facility was operated in Italy at one time to recover zinc

from an acidified waste stream from a plant manufacturing rayon by the viscose process.

Two variations of the technology are supported liquid membranes and emulsion type liquid membranes. Supported liquid membranes utilise a solid oleophilic polymeric membrane into which the organic phase has been absorbed. The aqueous feed solution passes on one side of the membrane and the aqueous strip solution passes on the other side. Transfer of the solute is facilitated by the extractant in the organic phase which is sandwiched between the two aqueous phases. This has been illustrated in Figure 2.

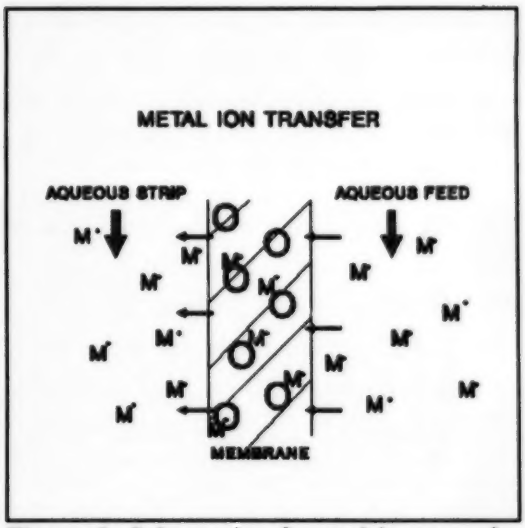


Figure 2: Schematic of metal ion transfer for a supported liquid membrane.

In the emulsion type of liquid membrane, a stable water-in-oil emulsion is created with the aqueous strip solution constituting the "water" in the organic phase "oil". This emulsion is contacted with and dispersed into the aqueous feed solution. The metal solute is extracted into the organic phase and then rapidly transferred to the aqueous strip phase within the organic globules. After separation from the raffinate, the emulsion is broken down electrostatically to provide a conventional electrolyte and stripped organic phase. Spent electrolyte and stripped organic are re-emulsified and recycled to the extraction stage.

Following is a summary of the literature cited for SLM. SLM has been investigated at the laboratory scale for the recovery of a number of metals. de Haan, Bartels and de Graauw (1989) investigated the recovery of copper ions using a capillary membrane module. The extractant used was LIX 84 at 10 - 40 volume % dissolved in either Kerosene or decane. The membrane used consisted of hydrophobic polypropylene capillaries in a polycarbonate housing. From their work, they were able to produce a mass transfer model which included diffusion as well as reaction rates.

Yonehara, Yamamoto, Matsuyama and Teramoto (1988) investigated two kinds of supported liquid membrane for the separation of gallium, indium and zinc. Specifically, they

were interested in the recovery of indium from zinc and gallium using bis (2,4,4 - trimethylpentyl) phosphinic acid and the separation of gallium and indium from zinc using 2 - bromodecanoic acid. Their results showed that the relevant selectivities were obtained but the permeation rates across the SLM's were lower than the theoretical calculations indicated. They attributed this to some co-extraction of zinc although they believed that selecting the right diluent might increase the separation factor.

Using a teflon filter membrane impregnated with trioctlyamine, Nishiki and Bautista (1986) were able to transfer Platinum (IV) from a hydrochloric acid solution to a sodium carbonate or sodium hydroxide solution. A high concentration factor (upto 60) was achieved. Further, the results showed that with low feed platinum concentrations and high TOA concentrations the permeation rate of the platinum through the membrane will be limited by the diffusion rate of platinum through the film on the feed side of the membrane.

As part of the research conducted by the Chemistry Division of Argonne National Laboratory into SLM technology and its applications, Chiarizia and Horwitz (1990) studied the removal of uranium from groundwater by supported liquid membranes. They determined that Cyanex 272 [bis (2,4,4 - trimethylpentyl) phosphinic acid] in n - dodecane was very effective in selectively recovering uranium (VI) versus calcium and magnesium from groundwater at pH 2. Further, they achieved concentration factors of 10^3 and demonstrated the independence of the uranium permeability coefficient from the uranium concentration in the range 10^{-3} - 0.5 M. The authors noted that stripping the organic phase at a concentration of 0.5 M U(VI) with 1 - hydroxy - ethane - 1, 1 - diphosphonic acid (HEDPA) required a 1 M solution of the stripping reagent and that this high a concentration might be detrimental to the membrane.

Fernandez, Aparicio and Muhammed (1987) were able to extract zinc using DEHPA supported in a polyvinylidene fluoride sheet. O'Hara and Bohrer (1989) were able to recover copper from spent etching solution using either teflon or polypropylene sheets containing LIX 54 - 100 (β - diketone) in Kerosene.

In a review of work on SLM's carried out by the Chemistry Division of Argonne National Laboratory, Pier Danesi (1985) noted that they had looked at SLM systems for Eu^{3+}, Cu^{2+}, Am^{3+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, and H^+. Much of this work has been used to develop models to describe the permeation of the metal ions through the membrane and

to derive suitable equations which account for the chemistry as well as the hydrodynamics and geometry of the system.

2.0 EXPERIMENTAL PROCEDURE

The experiments were performed with an MSX-500 ™ System from Sepracor Inc., Marlborough, Massachusetts, USA. The unit is a laboratory scale membrane - mediated solvent extraction system which contains a membrane module and ancillary equipment. The membrane module contains a large number of hollow tube fibres which are hydrophillic. The total membrane surface area is approximately 1.5 m^2. The rest of the unit contains two identical pumping systems with a positive displacement pump, flowmeter, membrane inlet and outlet pressure gauges, a pressure control valve and a pressure relief valve. One system pumps solvent to the lumen (inside the tubes) side of the module and the other system pumps solvent to the shell (outside the tubes) side of the module. The system is shown in Figure 3.

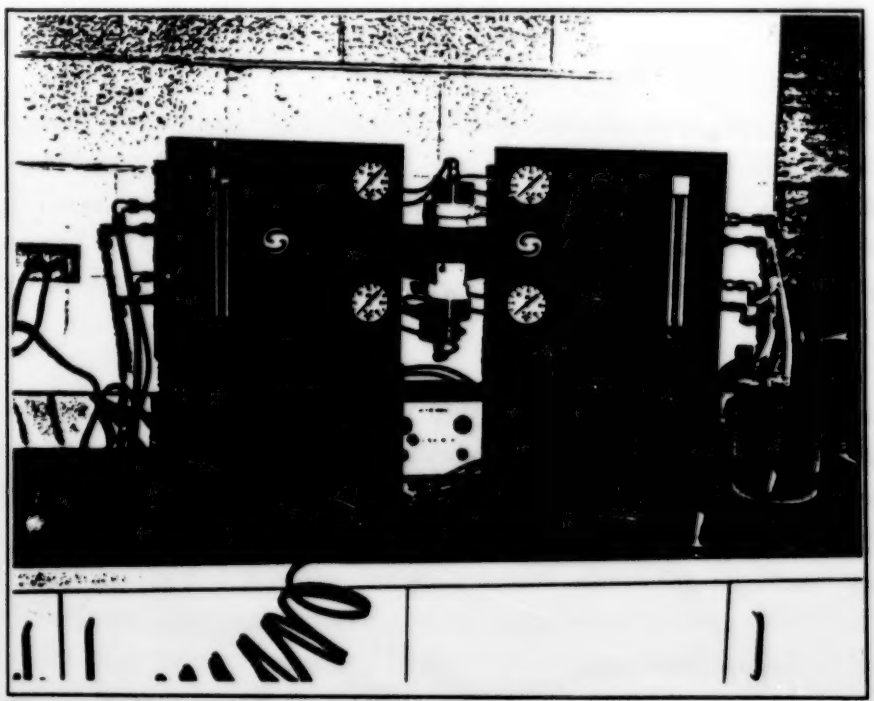


Figure 3: Photograph of membrane mediated test apparatus.

The feed solutions consisted of a synthetic acid mine drainage solution and a sample

of acid mine drainage from East - West Caribou Mining. The synthetic solution was prepared for preliminary testing such that the tenor of 980 mg/l Zn was approximately the same as the zinc content of a known AMD stream from a New Brunswick site. It was prepared by dissolving 4.34 g of Anachemia lab grade zinc sulphate in 1 litre of distilled water and adjusting the pH to 3.08 with H_2SO_4. The AMD sample from East-West Caribou Mining assayed 470 mg/l Zn, had a pH of 3.1 and contained a small amount of very fine iron oxides. The original intent was to use AMD from the site that the synthetic solution was based on, however, it was not possible to obtain a sample at the time of the testwork.

The organic phases were either Cyanex 302 dissolved in Exxsol D-80 Solvent or DEHPA dissolved in Kerosene. Cyanex 302 (active ingredient: bis (2,4,4-trimethylpentyl) monothiophosphinic acid) was provided by Cyanamid Canada Inc. and was used as received. The Exxsol D-80 Solvent was provided by Esso Chemical and is a C_{10} - C_{16} aliphatic light distillate hydrocarbon. The sample of DEHPA (di-2-ethylhexyl phosphoric acid) came from BDH and has a minimum purity of 96 %. The kerosene came form Irving Oil Ltd, Saint John. Stripping was carried out with either 40 g/l or 80 g/l H_2SO_4.

The literature review had indicated that DEHPA was the most common extractant for zinc and that kerosene was the usual diluent. The review also indicated that Cyanex 302 was a promising zinc extractant. The Cyanex 302 was usually diluted with Exssol D-80 Solvent. Since the testing at this stage was preliminary, and it was not known whether satisfactory results could be achieved, it was decided to test both extractants in case one did not give good results.

Concurrently with the testing of the supported liquid membrane unit, separatory funnel tests were conducted. These were standard tests which determined extractions for different amounts of extractant. In these tests, a given volume of aqueous feed was placed in a separatory funnel with a given volume of the organic phase. The separatory funnel was shaken for five minutes and then the two phases were allowed to separate. The aqueous feed and the raffinate were analyzed so that metal extractions could be calculated. Aqueous to organic ratios and per cent extractant in the organic phase were varied.

Operation of the SLM unit is relatively simple. The first step with a new unit is to clean out any contaminants such as excess plasticizers and to check the module for leaks in the membrane. The unit is operated so that the aqueous phase goes around the outside of

the fibres while the organic phase passes through the hollow fibre tubes. Since the membrane is hydrophillic, the aqueous phase is absorbed into the membrane. Therefore, to stop transfer of aqueous solvent into the organic phase, the organic phase must be pumped at a higher pressure than the aqueous phase.

In the initial experiments, the organic and aqueous phases were recirculated through the unit for thirty minutes. Samples of the aqueous phase were taken at set times. In later experiments, the aqueous phase was treated in the unit in a single pass. Using a modified experimental procedure, a technique for running a three stage counter-current extraction system was devised. Samples of acid mine drainage were treated in the membrane unit in single passes (no recirculation). Approximately half the aqueous material that was treated once was passed through a second time. The intent was to produce aqueous material suitable as feed to Stages 1, 2 and 3 of the three stage process. Each aqueous product was treated counter - currently with organic (50 % Cyanex 302 in Exxsol D-80 Solvent).

3.0 RESULTS AND DISCUSSION

3.1 Separatory Funnel Tests

In these tests the volume percent of Cyanex 302 in Exxsol D-80 diluent was varied from 5 % to 40 %. In each test, 50 ml of aqueous and 50 mls of organic were shaken together. These tests were repeated using DEHPA in Kerosene. Recoveries were calculated by subtracting the final concentrations from the feed concentrations and dividing that number by the feed concentrations. The tests were conducted with both the synthetic AMD and the AMD from the field.

The results of all these tests, which are presented in Table 1, show that good zinc recoveries of 99% were obtained. Cyanex 302 appears to be a stronger extractant than DEHPA in that the recovery with DEHPA for a given % extractant in diluent is lower than with Cyanex 302. Recovery with Cyanex 302 appears to be related to metal concentration because the recoveries at the lower feed concentration are consistently higher than the equivalent recoveries at the higher feed concentration. This does not appear to be true for DEHPA.

TABLE 1

RESULTS OF SEPARATORY FUNNEL TESTS

A/O ratio: 1
Organic volume: 50 mls
Contact time: 5 minutes
Temperature: ambient

% EXTRACTANT	SYNTHETIC SOLUTION % ZN EXTRACTION		FIELD SAMPLE % ZN EXTRACTION	
	CYANEX 302	DEHPA	CYANEX 302	DEHPA
5	75.7		90.6	83.6
10	94.5	89.7	98.2	90.7
15	98.0		99.3	92.8
20	98.8	95.6	99.6	94.4
40	99.4			

3.2 Supported Liquid Membrane Unit Tests

Initially, the aqueous to organic ratio was set at 2, ie: the volume of organic at 250 ml was half the volume of aqueous at 500 ml. Cyanex 302 was diluted to a 10 % by volume solution with Exxsol D-80 Solvent and DEHPA was diluted to a 20 % by volume solution with Kerosene. Both the organic and aqueous phases were circulated through their respective sides of the membrane for 30 minutes at a flowrate of approximately 500 ml/min. Samples for analysis of the aqueous phase were taken at 1,2,4,7,10,15,20 and 30 minutes.

The results of these tests are presented in Tables 2 and 3. In Table 2, the aqueous feed was a sample of acid mine drainage which contained approximately 470 mg/l Zn. In Table 3, the aqueous feed was the synthetic zinc solution which contained 970 mg/l Zn.

As with the separatory funnel tests, Cyanex 302 appears to be the stronger extractant. Zinc extractions with Cyanex 302 were 95% after 30 minutes while the zinc extractions with DEHPA were 90%. Factors which might affect this include contact time, per cent extractant in the organic phase and the aqueous to organic ratio. A comparison of the results in

Tables 2 and 3 indicated that metal concentration in the aqueous phase has an effect on extraction rates when using Cyanex 302.

Samples of each aqueous feed and raffinate for the three stage counter-current simulation were collected for analysis. The results which are shown in Table 4 are not

TABLE 2
RESULTS OF SLM TESTS USING AMD

A/O ratio: 2
Sample: Acid mine drainage, 470 ml g/l Zn
Organic Volume: 250 ml

TIME - MINUTES	CYANEX 302 % Zn EXTRACTION	DEHPA % Zn EXTRACTION
0	0	0
1	46.4	40.0
2	53.6	46.1
4	62.4	54.7
7	72.8	65.7
10	80.5	71.7
15	87.0	81.1
20	91.1	85.3
30	95.1	89.7

very conclusive. Analysis of the actual Zn concentrations in the aqueous phases indicated that insufficient zinc was extracted during the initial preparation of the aqueous feeds for stages 2 and 3. The results indicate that more contact time and/or a larger membrane area is required.

3.3 Stripping Tests

Some preliminary stripping tests were conducted using the membrane module. In the first of these tests, the final organic solution from the three stage counter - current extraction experiment was contacted with an approximately equal volume of 40 g/l H_2SO_4.

In the remaining stripping tests, the organic used during the preparation of the aqueous feeds for the different stages in the three stage counter - current extraction experiment was divided into two samples of approximately 200 ml each. These were stripped in the first test with 40 g/l H_2SO_4 and in the second test with 80 g/l H_2SO_4. For all three tests, the organic and aqueous phases were circulated for 10 minutes and samples of the aqueous phase were taken at 1, 2, 4, 7, and 10 minutes.

The results of these tests are shown in Table 5. A comparison of the results for the last two tests indicates that recovery is faster with the 80 g/l H_2SO_4. In neither case, however, was the stripping recovery very high. At 40 g/l H_2SO_4 the Zn recovery after 10 minutes was 3.6 % and at 80 g/l the zinc recovery was 6.7 %. Iron recovery increased by 4.3 times with the stronger acid.

TABLE 3
RESULTS OF SLM TESTS USING SYNTHETIC AMD

A/O ratio: 2
Sample: Synthetic acid mine drainage, 970 mg/l Zn
Extractant: 10 % Cyanex 302 in Exxsol D-80
Organic Volume: 250 ml

TIME, MINUTES	% Zn EXTRACTION
0	0
1	27.3
2	32.8
4	42.3
7	50.8
10	55.2
15	62.3
20	65.6
30	71.0

TABLE 4
RESULTS OF THREE STAGE TEST

Extractant: 50 % Cyanex 302 in Exxsol D-80
Organic Volume: 300 ml
A/O Ratio: 10:1

	% Zn Extraction	Zn mg/l	
		Start	Finish
First step (pregnant aqueous)	19.9	423	339
Second Stage	12.8	384	335
Third Stage (fresh organic)	12.3	375	329
Overall	38.7		

TABLE 5

RESULTS OF STRIPPING TESTS

Organic: 50% Cyanex 302 in Exxsol D-80
A/O Ratio: 1:1
Organic Volume: Organic 1 - 300 ml; Organic 2 - 200ml
Strip Phase: 40 g/l or 80 g/l H_2SO_4

TIME min.	ORGANIC 1		ORGANIC 2			
	40 g/l H_2SO_4		40 g/l H_2SO_4		80 g/l H_2SO_4	
	Zn mg/l	Fe mg/l	Zn mg/l	Fe mg/l	Zn mg/l	Fe mg/l
1	46.4	34.0	5.00	5.53	4.27	29.3
2	48.6	36.5	4.72	6.48	4.89	32.0
4	50.2	37.6	5.56	7.67	6.89	35.6
10	54.5	35.4	7.66	9.51	14.3	41.

Information on stripping subsequently supplied by Cyanamid indicates that the zinc should be readily stripped by a strip solution containing 200 g/l H_2SO_4. Their data showed a recovery of 92 % in a single stage with an O/A ratio of 5. These results indicate that a stronger acid is required.

4.0 PRELIMINARY REVENUES AND COSTS

4.1 Introduction

Limited cost data (capital and operating) has been presented in the literature. This data is specifically for copper although many costs should be similar for other metals.

The major capital costs for the solvent extraction section of a plant are for mixer - settler equipment; various storage vessels, piping and pumps; and the inventory of extractant and diluent. Typical capital costs in US$ (1986) are 1 800 - 2 500 / m^2 of settler area. Capital costs for the electrowinning section include the costs for the electrowinning cells including liners and supports; the tankhouse building; electrode handling equipment; ancillary equipment; and the electrical system. These costs are directly related to copper production and range from US$ (1986) 800 - 1 100 per annual ton of copper.

Operating costs are calculated to be approximately US$ (1986) 0.30 per pound of copper produced. These costs include power, most of which is used in electrowinning; replacement of material particularly reagents; labour and maintenance. Power costs are about 44 % of the operating costs and supplies are approximately 28 %. Labour and maintenance contribute approximately 50 % each of the remaining operating costs.

In terms of labour requirements, MQN in Bilbao operated the whole Zincex plant with 22 people.

The most significant factor affecting both the capital and operating costs for an SLM system is the flowrate per unit area number. Doubling this figure would reduce the capital costs by approximately 40 % and the operating costs could be almost halved. Membrane life also has a significant effect on the operating costs.

Other factors which could affect the choice of whether to use SLM include reduced reagent requirements for effluent treatment, easier handling of the effluent streams and enhancement of environmental accountability.

4.2 Revenues

An annual revenue for zinc recovered from New Brunswick acid mine drainage has been estimated based upon the following data which is an average of several sites:

Flowrate	=	1400 litres / minute
Zn Assay	=	900 mg / litre
Annual production (@ 95 % recovery)	=	630 tonnes / year
Potential Revenue (@ US $0.60 / lb)	=	US $0.83 x 106

(@ C $1.15/ US $1.00) = C $0.95 x 106

4.3 Capital Cost

Preliminary estimated capital costs have been calculated. Membrane requirements were determined using a vendor supplied factor of 1 litre/min/m^2 of membrane which was determined from the preliminary laboratory results. The turn-key capital cost for the membrane system has been quoted at C $ 2750 / m^2. Costs for electrowinning of $1300 / tonne of metal produced were obtained from the literature. Start up reagent requirements have been estimated using linear scale - up from the laboratory.

Based on the above the total preliminary capital cost for a system to treat 1400 litres/day is estimated as follows:

Membrane requirements	1 400 m^2
Turn-key cost of system	$3.9 x 10^6
Electrowinning capital costs	$0.4 x 10^6
Start-up reagent costs	$0.1 x 10^6
TOTAL CAPITAL COST	$4.4 x 10^6

4.4 Operating Costs

Membrane replacement costs have been quoted at $550 / m^2. Therefore, for 1400 m^2 the replacement cost is $0.8 x 10^6.

Based upon Sepracor's experience in other application areas total membrane replacement each year has been assumed and using Sepracor's estimates that this is 80 % of the unit operating cost. total membrane system operating cost = $1 x 10^6.

Electrowinning operating costs have been derived from costs for electrowinning copper and estimated as $220 / tonne of metal produced. Electrowinning operating costs = $0.07 x 10^6

TOTAL OPERATING COSTS = $1.1 x 10^6

5.0 CONCLUSIONS

The survey of the published literature and manufacturer's information indicated that using supported liquid membrane technology to recover zinc from zinc bearing streams should be feasible. In addition, the following two potential extractants were identified:

Cyanex 302 - bis(2,4,4-trimethylpentyl) monothiophosphonic acid
DEHPA - di-2-ethylhexyl phosphoric acid

The preliminary laboratory testwork demonstrated that using a membrane mediated solvent extraction system to recover zinc from acid mine drainage streams was technically feasible. In particular,

* 95% of the zinc was removed from an acid mine drainage stream from northern New Brunswick using membrane mediated solvent extraction and Cyanex 302 dissolved in Exxsol D-80 Solvent
* Cyanex 302 removed more zinc from the acid mine drainage samples than DEHPA under equivalent experimental conditions
* A/O ratios of 1 and 2 gave high recoveries
* Both Cyanex 302 and DEHPA are satisfactory extractants for zinc
* Strip solutions containing 40 and 80 g/l H_2SO_4 did not provide adequate stripping. Vendor information indicates good recoveries with a strip solution containing 200 g/l H_2SO_4.
* Separatory funnel tests demonstrated that the higher the per cent extractant (upto 40%) in the organic phase, the higher the zinc removal from the aqueous feed for the same experimental conditions
* Preliminary capital costs are estimated as $\$4.4 \times 10^6$
* Preliminary operating costs are estimated as $\$1.1 \times 10^6$
* Revenue for a 1400 litre/min stream containing 900 mg/l of zinc is $\$0.95 \times 10^6$.

6.0 RECOMMENDATIONS

Although the laboratory testwork completed to date has demonstrated that supported liquid membrane technology can be used to recover at least zinc from acid mine drainage, more laboratory testwork should be carried out to further define the operating parameters and relationships between the separatory funnel results and the membrane module test results. Parameters which require better definition are acidic strength of the stripping solution, per cent extractant in the organic phase when used with the membrane module, the aqueous to organic ratios for extraction and stripping and flowrates through the membrane module.

Once these parameters have been investigated further, it should be possible to select an optimum set of conditions for operating the system. Also, it will be possible to refine the capital and operating costs.

7.0 REFERENCES

Chiarizia, R. and Horwitz, E.P., "Study of Uranium Removal from Groundwater by Supported Liquid Membranes", Solvent Extraction and Ion Exchange, 8(1), pp 65-98, 1990

Danesi, P.R., and Bohrer, M.P., "Supported Liquid Membranes for Copper Transport", Journal of Membrane Science, 44, pp 1577-1595, 1987

de Haan, A.B., Bartels, P.V. and de Graauw, J., "Winning Zinc through Solvent Extraction and Electrowinning", E&MJ, October, pp 92-94, 1979

Fernandez, L., Aparicio, J. and Muhammed, M., "The Role of Feed Metal Concentration in the Coupled Transport of Zinc through as Bio- (2-ethlyhexyl) phosphoric Acid Solid Supported Liquid Membrane from Aqueous Perchlorate Media", Separation Science and Technology, 22(6), pp 1577-1595, 1987

Nishiki, T. and Bautista, R.G., "Transport of Platinum (IV) Through Supported Liquid Membrane Containing Trioctylamine Carrier"

O'Hara, P.A. and Bohrer, M.P., "Supported Liquid Membranes for Copper Transport", Journal of Membrane Science, 44, pp 273-287, 1989

Yonegara, T., Yamamoto, A., Matsuyama, H. and Teramoto, M., "Separation of Ga, In and Zn by Supported Liquid Membranes," Proceedings of Symposium on Solvent Extraction, Faculty of Engineering Design, Kyoto Institute of Technology, Kyoto, Japan, pp 151-156, 1988

APPENDIX A

A Discussion of Solvent Extraction

SOLVENT EXTRACTION

1.0 Introduction

The original work on solvent extraction was carried out in the 1940's when the nuclear - materials industries of the US and Britain were seeking ways to recover uranium from its ores and to separate plutonium from uranium and its fission products (Bailes, Hanson and Hughes, 1976). With discoveries of new extractants and improvements in existing ones, solvent extraction was investigated for the recovery of other valuable metals such as rare earths, zirconium, hafnium and vanadium.

By the early 1960's nickel, copper and cobalt were being considered for recovery by solvent extraction. In 1968 the first copper solvent extraction electrowinning plant was commissioned by Ranchers Mining Company at its Bluebird property in Arizona (Townsend and Severs, 1990). Since then, with chemical, mechanical and operational improvements solvent extraction has become the cheapest method for producing grade A copper and approximately 700 000 tonnes per year are produced this way.

The recovery of copper from low grade ores and scrap and the recovery of uranium are the major industrial solvent extraction operations. Nickel, cobalt and zinc are recovered by as well. The SEC Corporation plant in El Paso, Texas recovered nickel from a copper electrolyte bleed stream using LIX 64N at an alkaline pH. The separation of cobalt from nickel has been practised at many plants treating superalloy and other nickel - rich alloy scrap. (Jackson, 1986).

Tecnicas Reunidas SA in cooperation with Union Explosivos Rio Tinto SA (UERT) and Metalquimica del Nervion SA (MQN) developed a process to recover zinc from pyrite cinders (Nogueria, Regife and Arocha, 1979). MQN has operated a plant using the "Zincex" process since 1976. The plant capacity is 8 000 tonnes per year of slab zinc. Feed to the Zincex plant comes from leaching zinc bearing pyrite cinders which have undergone a chloridizing roast. The feed stream contains 20 - 30 gpl zinc, 18 - 25 gpl iron, 70 - 100 gpl chloride, 120 - 155 gpl sulphate and copper, cadmium, cobalt, nickel, arsenic, manganese and other elements. Free chloride in excess of 1N is required for efficient zinc extraction. In the first stage extraction, a secondary amine is used to extract the anionic zinc chloride ion. The extraction is:

$$2\ R_2\ NH_2\ Cl\ +\ Zn\ Cl_4^{=}\ =\ (R_2\ NH_2)_2\ Zn\ Cl_4\ +\ 2\ Cl^-$$

The zinc is stripped with water. Metals which form complex chloride anions such as copper, cadmium, cobalt and ferric iron, will be partially co - extracted with the zinc.

In a second extraction stage, the zinc cation is extracted using di - 2 - ethyl hexyl phosphoric acid (DEHPA) in Kerosene. Careful pH control to maintain a level of 2.2 to 2.8 is required to selectively extract the zinc. The final zinc electrolyte contained 50 - 60 gpl zinc, 20 ppm iron, 30 ppm chloride and less than 1 ppm of metallic impurities. 99.99% electrolyte zinc was recovered using lead anodes and aluminum cathodes in the electrowinning section.

Another application of solvent extraction for zinc recovery, was the recovery of zinc from effluent streams from plants manufacturing rayon by the viscose method. The zinc was selectively extracted against calcium from a sulphate effluent stream at pH 1-2. The recovered zinc was recycled to the viscose process acid bath.

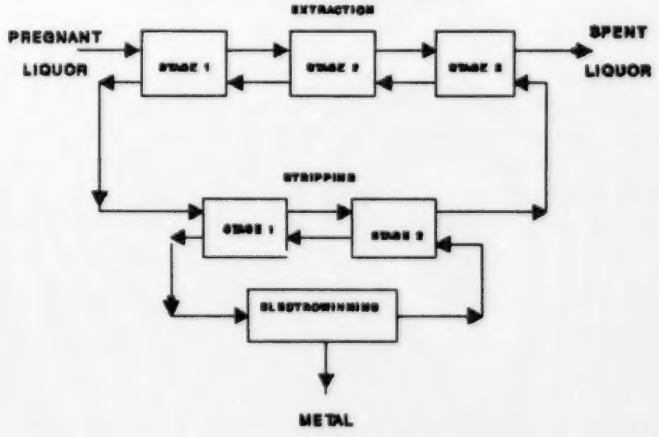
1.1 Theory

1.1.1 Introduction

A schematic diagram of solvent extraction - electrowinning is shown in Figure 1. The aqueous pregnant liquor passes through a number of stages where it counter-currently contacts the organic phase. The element(s) being recovered transfer to the organic phase. The raffinate is recycled to the leach circuit.

The loaded organic phase passes to a second series of contactors where it is counter-currently contacted with a second aqueous phase. The extracted element(s) pass from the organic to the aqueous phase. The organic is recycled to the extraction step and the aqueous phase goes to metal recovery. Spent electrolyte returns to the stripping stage.

FIGURE 1
SOLVENT EXTRACTION CIRCUIT



For extraction to be successful, the organic and aqueous phases must be immiscible and the organic extractant must be able to combine with the element(s) being recovered to bring them into the organic phase. Establishment of an equilibrium of a solute between two immiscible liquids is defined in terms of the partition law. When a solute is a dissolved in immiscible liquids A and B in contact, the free energy (G_i) of the solute in each is in equilibrium. Thus

$$G^{\circ}_{A} + RT \ln a_{A} = G^{\circ}_{B} + RT \ln a_{B} \qquad (1)$$

Where R = Recovery Factor
T = Temperature
A = Relative Active

or

$$\ln \frac{a_B}{a_A} = \frac{G^\circ_A - G^\circ_B}{RT} \quad (2)$$

At temperature T, G°_A and G°_B are constants for a given solute in a given solvent, therefore,

$$\ln \frac{a_B}{a_A} = \text{constant} \quad (3)$$

and

$$\frac{a_b}{a_A} = P^\circ \quad (4)$$

Where P° = partition constant

The value of the partition constant is influenced by the nature of the solute, the solvents and the temperature, Further, equation 4 is only valid for one particular solute species which is common to both solvents. It is not valid for any associated species that are not involved in the activity ratio.

In hydrometallurgical operations the distribution of total metal values in each solvent is very important. Therefore, the distribution ratio (D), is more useful and it is given as follows:

$$D = \frac{\Sigma[M]_o}{\Sigma[M]_{aq}} \quad (5)$$

Where $\Sigma[M]_o$ refers to the total given metal content of the organic phase and $\Sigma[M]_{aq}$ refers to the total content of the same metal in the aqueous phase. Thus, when a volume V_o of organic solvent equilibrates with a volume V_{aq} of aqueous solvent, the fraction of metal recovered into the organic solvent, R, is given by:

$$R = \frac{D}{D + (V_{aq} / V_o)} \quad (6)$$

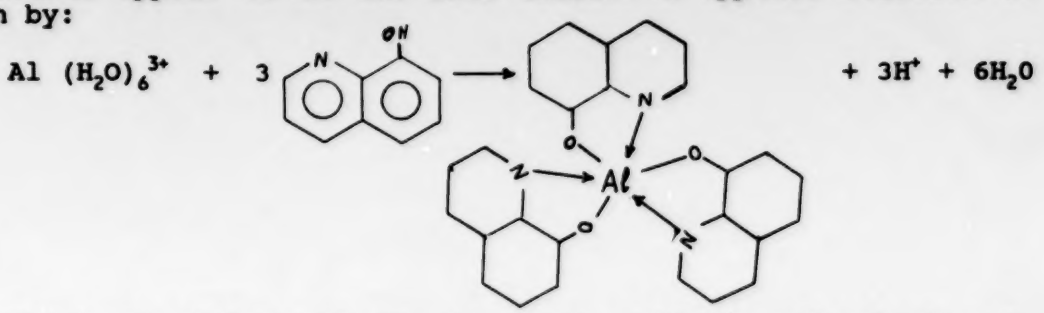
1.1.2 Extraction Mechanisms

Metals in aqueous solutions are generally there in an ionic form. The organic solvents are usually covalent in character. Therefore, to effect a transfer of the metal species from the aqueous phase to the organic phase it is necessary to achieve charge neutralization and to replace solvating water molecules with covalent type ligands. This can be achieved in three different ways

- by the formation of uncharged co-ordination compounds
- by ion exchange processes
- by solvation with ion association

Uncharged co-ordination compounds are formed when complexing agents with excess electron pairs combine with metal ions with election pair deficiencies. Chelating agents are the most important reagent of this type. They tend to be soluble in non-polar solvents and insoluble in aqueous solvents. Five or six membered ring

structures appear to be the most stable. A typical reaction is given by:



Two types of ion exchange can occur, cationic and anionic. In cationic processes metal cations exchange places with hydrogen ions from the extractant. Examples of this type of reagent are organic acids such as alkyl phosphoric acids and carbonic acids. The extraction of zinc with versatic acid is a typical reaction.

$$2R_1\ R_2\ CH_3\ COCOOH + Zn^{2+} = (R_1\ R_2\ CH_3\ COCOOH)_2\ ZN + 2H^+$$

Anionic exchange takes place through the replacement of anions from long chain alkyl amines by complex metal anions. The extraction of platinum from acid chloride solutions by tri - octyl amine illustrates this type of extraction reaction.

$$R_3\ N + HCl = R_3\ NH.Cl$$

and

$$2R_3\ NH.Cl + PtCl^{2-}_6 = (R_3\ NH)_2\ Pt\ Cl_6 + 2\ Cl^-$$

Solvation occurs through the replacement of solvating water molecules in an aquo - cation by organic solvent molecules. Ethers, esters and ketones fall into this category. This type of reaction can be illustrated by the dimethyl ether extraction of iron from a chloride solution. The first step is anion formation which is induced by high chloride concentration.

$$Fe\ (H_2O)_{63+} + 4Cl_{-} = Fe\ (H_2O)_2\ Cl^{4-} + 4H_2O$$

In the second step solvation by diethyl ether yields

$$Fe\ [\ (C_2H_5)_2\ O\ ]_2\ \ Cl^{4-}$$

At the same time protonation of the diethyl ether by oxonium ions yields

$$(C_2H_5)_2\ O + H^+_3O = (C_2H_5)_2\ OH^+ + H_2O$$

Electrostatic attraction between the positive and negative ions produces charge neutralisation which, along with removal of the solvating water molecules, favours transfer to the organic phase.

1.1.3 Extraction Equilibria

The equilibrium mechanisms involved in the extraction process are somewhat determined by the type of solvent being used. For chelating agents represented by RH a chelate R_2M forms with metal

ions M^{2+}. R_2M and RH are the only components soluble in the organic phase. In the aqueous phase

$$RH = R^- + H^+ \quad ; \quad K_D = \frac{[R^-]_{aq}\,[H^+]_{aq}}{[RH]_{aq}} \tag{7}$$

and

$$2R^- + M^{2+} = R_2M \quad ; \quad K_{STAB} = \frac{[R_2M]_{aq}}{[R^-]^2_{aq}\,[M^{2+}]_{aq}} \tag{8}$$

From equation 4, the relevant partition coefficients are

$$P_{RH} = \frac{[RH]_o}{[RH]_{aq}} \tag{9}$$

and

$$P_{R2M} = \frac{[R_2M]_o}{[R_2M]_{aq}} \tag{10}$$

From these it can be seen that the distribution ratio (Equation 5) is

$$D = \frac{[R_2M]_o}{[R_2M]_{aq} + [M^{2p}]_{aq}} \tag{11}$$

Assuming that $[R_2M]_{aq}$ is negligible and substituting with Equations 9 and 10 gives

$$D = \frac{K_{STAB} \times P_{R2M} \times K^{2p} \times [RH]^2_o}{P_{RH} \times [H^+]2_{aq}} \tag{12}$$

This equation shows that the distribution ratio is governed by the partition coefficient and dissociation constant of the extractant as well as the partition coefficient of the chelate. If all these constants are combined into a single constants K' then Equation 18 can be simplified to

$$\text{Log } D = \log k' + 2 \log [RH]_o + 2\,pH_{aq} \tag{13}$$

Equation 13 shows that D is affected by the concentration of the extractant in the organic phase and the pH of the aqueous phase. If D is plotted against pH it is found that there is an inflexion point where D increases significantly. At this point D = 1 and the pH value is given the subscript 0.5. At pH values greater than pH 0.5 extraction takes place. Selective extraction can be achieved when pH 0.5 for M_1 is different from pH 0.5 for M_2.

Since cationic ion exchange processes are controlled by the hydrogen ion level, the equilibrium mechanisms are likely to be similar to the chelating reagents.

Since there are many systems which use solvation, it is difficult to give a general approach to the equilibrium reactions. Equilibrium constants can be derived; K_1 for uncharged species in

the aqueous phase and K_2 for solvated species. Substitution of the distribution ratio into the product of K_1 x K_2 results in

$$\log D = \log K_1 K_2 + 2 \log [\text{acid ion}]_{aq} + n \log [\text{extractant}]_o \quad (14)$$

For the extraction of uranium by tri - butyl phosphate (TBP) from a nitrate aqueous phase Equation 14 reads

$$\log D = \log K_1 K_2 + 2\log [NO^{-3}]_{aq} + n \log [TBP]_o$$

and

$$K_1 = \frac{[UO_2 (H_2O)_4 (NO_3)_2]_{aq}}{[UO_2 (H_2O)^{2-}_6]_{aq} \times [NO^{-3}]^2_{aq}}$$

and

$$K2 = \frac{[UO_2 (H_2O)_4 \cdot n (NO_3)_2 (TBP)_n]_o}{[UO_2 (H_2O)_4 (NO_3)_2]_{aq} \times [TBP]^n_o}$$

n is the solvation number and it is the average number of solvent molecules per molecule of extracted species. The distribution ratio indicates that high acid ion concentration and high organic extractant concentration should result in a high extraction.

1.1.4 Extraction Kinetics

Although no single theory of extraction is satisfactory for all transfer mechanisms, the two-film theory has proven to be the most useful for determining factors affecting extraction rates. In the two-film theory, the rate of transfer of the metal from one phase to the other is controlled by how much the metal concentrations in each phase differ from the equilibrium values. On either side of the interface a concentration gradient exists such that at the interface the aqueous and organic concentrations are lower.

For a metal solute transferring from the aqueous phase to the organic phase the rate of mass transfer in the aqueous phase towards the interface is given by

$$\frac{dn}{dt_{aq}} = K_{aq} A (C_{aq} - C_{aqo}) \quad (15)$$

and the rate of mass transfer in the organic away from the interface is given by

$$\frac{dn}{dt_o} = K_o A (C_o - C_{oo}) \quad (16)$$

where A = area of interface
K_i = film mass transfer coefficient
C_i = relevant concentrations for bulk solvents
C_{io} = relevant concentrations at interface

Under steady state conditions the rate of extraction =

$$\frac{dn}{dt} = K_{aq} A (C_{aq} - C_{aqo}) = \frac{dn}{dt_o} = K_o A (C_o - C_{oo}) \quad (17)$$

Since the film mass transfer coefficient includes factors for diffusivity of the solute and film thickness, it can be seen that agitation has the greatest effect on extraction rates. Agitation decreases the film thickness on both sides of the interface and it can also increase the interfacial surface area through more intimate mixing of the phases. It should be noted that there are practical limitations to the fineness of droplet sizes in that the two phases must separate after mixing and the coalescence rate decreases with finer droplet sizes. Further, with too fine droplet sizes a stable emulsion could be formed.

1.2 Extractants

From the published literature and information provided by the suppliers who were contacted, a number of products have been identified as possible zinc extractants. These have been included in Table 1.

TABLE 1

LIST OF POSSIBLE ZINC EXTRACTANTS

Secondary amines	Alamine 336 from Henkel Corp.
DEHPA	Di-2-ethylhexyl phosphoric acid
DTPPA	
Tridodecylamine - Triethlybenzene	
Versatic acids	R_1 R_2 CH_3 COCOOH
Tertiary high molecular weight amines	
LIX 860	5- dodecylsalicylaldoxime
Cyanex 272	bis (2,4,4- trimethylpentyl) phosphinic acid
Cyanex 301	bis (2,4,4- trimethylpentyl) dithiophosphinic acid
Cyanex 302	bis (2,4,4- trimethylpentyl) monothiophosphinic acid
TOPO	trioctylphosphine oxide
Trialkylphosphine oxide	

In general terms an extractant should meet certain requirements such as:

- selectively extracts the desired metal
- immiscible with aqueous phase

- permits easy stripping of the metal
- stability in the system

In addition, for the treatment of waste streams, the extractant must be able to achieve the desired metal extraction without pH adjustment.

In addition to the extractant, the organic phase contains a diluent or carrier solvent and may contain a modifier, The diluent which is usually a low cost, hydrocarbon product is used to lower the viscosity of the organic phase and to facilitate contacting between the aqueous and organic phases. To be used as a diluent, the product must meet certain requirements

- the ability to keep in solution complexed and uncomplexed extractant
- immiscibility with the aqueous phase
- as high a flash point as possible and as low an evaporation rate as possible
- chemical stability

These diluents are by - products from the production of chemicals or other hydrocarbon products from petroleum feedstock. Therefore, they can be quite complex mixtures which meet certain basic requirements eg: y_1 - y_2 % of C_x carbon chain length product or a given minimum flashpoint. Generally, these products have been considered as inert materials in the system. Although they have some influence on extraction rates, equilibrium points and coalescing rates very little work seems to have been done in this area. (This may in part be that because they are by - products, a given product can vary quite considerably in its content). One aspect that has received some attention is aliphatic versus aromatic content. It has been shown that in the extraction of copper using oximes the loading of copper is improved with a higher aromatic content while higher aliphatic contents give increased mass transfer rates.

1.3 Circuit Design

Extraction could be carried out using either cross - current or counter - current contacting. Cross - current extraction would be a batch process where a give volume of fresh organic is equilibrated with the aqueous phase at each stage. Assuming that the concentration of metal remaining in the aqueous phase after n equilibrations is given by

$$\Sigma[M_{aq}]_n = \Sigma[M_{aq}]_o \times \left(\frac{V_{aq}}{V_{aq} + DV_o}\right)^n$$

where $[M_{aq}]_o$ is the initial metal concentration, it can be seen that maximum extraction is obtained by using small volumes of organic in a large number of equilibration stages. Such a system would not be practical.

Counter - current contacting involves equilibrating the loaded organic phase with incoming aqueous feed and equilibrating fresh organic with the almost spent aqueous phase. Such a system provides low solute concentration in the raffinate and high solute

concentration in the organic phase. Further, counter - current contacting can be operated continuously rather than in batches.

In practice, a typical extraction or stripping circuit consists of a number of mixer - settlers in series. Some typical design data quoted by Townsend and Severs (1990) is given below in Table 2.

TABLE 2

TYPICAL DESIGN DATA

Mixer residence times	1.5 to 3 minutes
Specific settler flowrate	2.9 to 8.6 m^3 / h / m^2
Number of extraction stages	1 to 6
Number of striping stages	1 to 3
O/A ratio in extraction	1 - 3.5 : 1
V/O extractant in organic phase	2 to 30

The number of extraction or stripping stages as well as solute concentrations in the organic and aqueous phase at each stage can be obtained theoretically through an extraction equilibrium diagram or McCabe - Thiele diagram. Figure 2 illustrates such a construction. The line OX is referred to as the distribution isotherm or equilibrium line and it has a slope which is the distribution ratio, D. Line AB is the operating line and is a plot of the metal concentrations in the aqueous and organic phases. The gradient of this line is the reciprocal of the phase ratio.

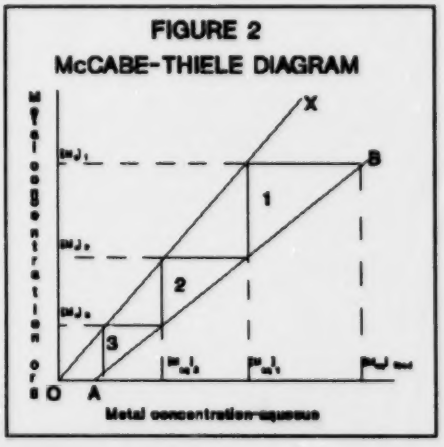


FIGURE 2

McCABE-THIELE DIAGRAM

The number of stages and the relevant aqueous and organic phase metal concentrations are obtained by taking the aqueous feed concentration where it meets line AB and then taking the obtained value of metal in the organic phase across to where it meets line OX. The aqueous phase metal concentration for stage 1 is followed down until it meets line AB. The procedure is repeated until adding more extraction stages does not provide further benefit. In Figure 2, three stages of extraction are required.

REFERENCES

Baites, P.J., Hanson, C. and Hughes, M.A., "Liquid - Liquid Extraction: Metals", Chemical Engineering, August 30, pp 86-94, 1976

Jackson, E., "Hydrometallurgical Extraction and Reclamation", Ellis Horwood Limited, Chickester, England, p 135, 1986

Nogueria, E.D., Regife, J.M. and Arcocha, A.M., "Winning Zinc Through Solvent Extraction and Electrowinning", E&MJ, October, pp 92-94, 1979

Prior, A., "Possibilities of Using Ion Exchange Membrane in the Recovery and Processing of Precious Metals", Precious Metals 1987: Proceedings of the Eleventh International Precious Metals Institute Conference, Brussels, Belgium, Ed. Vermeylen, G. and Verbecck, R., pp 485-493, 1987

Townsend, B. and Severs, K.J., "The Solvent Extraction of Copper a Perspective", Mining Magazine, January, 99 26-35, 1990